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Measurements on laboratory core-scale sediment/hydrate samples to predict reservoir behavior

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To accurately predict natural gas recovery from reservoirs containing gas hydrates, knowledge of both the reservoir properties and the properties and processes of the hydrate dissociation is required. Data acquired from measurements on both natural and laboratory samples are needed to appropriately bound parameters used in modeling. We have developed a new technique to produce core-scale gas hydrate/sediment samples that facilitates understanding reservoir-scale hydrate processes. These core-scale samples bridge the gap between small homogeneous samples adequate for performing fundamental thermodynamic property measurements, and reservoir-scale processes that require an understanding of the coupling of heat and mass transport. Investigations are performed to evaluate how depressurization or thermal stimulation may eventually be used to economically recover gas from naturally occurring hydrates using core-sized samples monitoring thermal gradients and mass fluxes.

Laboratory-made samples can be produced in various configurations to provide ranges for parameters used in modeling predictions. Hydrate configurations observed in natural samples can be made in the laboratory. These include disseminated, with the hydrate finely disseminated throughout the sample; nodular, with hydrate nodes up to ~5 cm in diameter; layered, with hydrate layers interspersed between porous medium layers possibly containing dispersed hydrate; and massive (Sloan, 1998). The most repeatable technique used for making hydrates in the laboratory is the method of Stern et al., (1998) in which small grains of ice are melted in the presence of a guest molecule (e.g. methane) at high pressure. The resulting porous hydrate can be compressed into nearly nonporous masses suitable for making thermodynamic and physical property measurements. Hydrate made in this fashion has also been ground and mixed with mineral grains to simulate hydrate in a porous medium. Using this technique, investigations using three possible hydrate configurations (nonporous, porous, and mixed with mineral grains) have provided significant information, however; other techniques are also needed to simulate the range of hydrate configurations found in nature.

We have made disseminated methane hydrate in a porous medium while attempting to maintain the mineral grain-to-grain contact that would be expected in a porous medium

under a significant lithostatic load. We start with a sand, partially saturate it with water, and compact it into a vessel in which we maintain control over pressure and temperature. We bring our sample into the hydrate stability region (typically 7 to 10 MPa and 3 to 5°C), and allow the hydrate to form from water held by capillarity in pendular rings and films. The typical time for hydrate to form is 24 hours. Hydrate in this configuration may increase the thermal conductivity of the porous medium despite its lower thermal conductivity, because the hydrate and mineral grains act in parallel. In contrast, in a sample with hydrate grains (or layers) interspersed between mineral grains (or layers), the overall thermal conductivity of the porous medium would be decreased. Our samples range in size, with our largest currently being 10.2 cm diameter and 11 cm in height (Figure 1), however other vessels are in preparation for making larger samples for other hydrologic measurements.

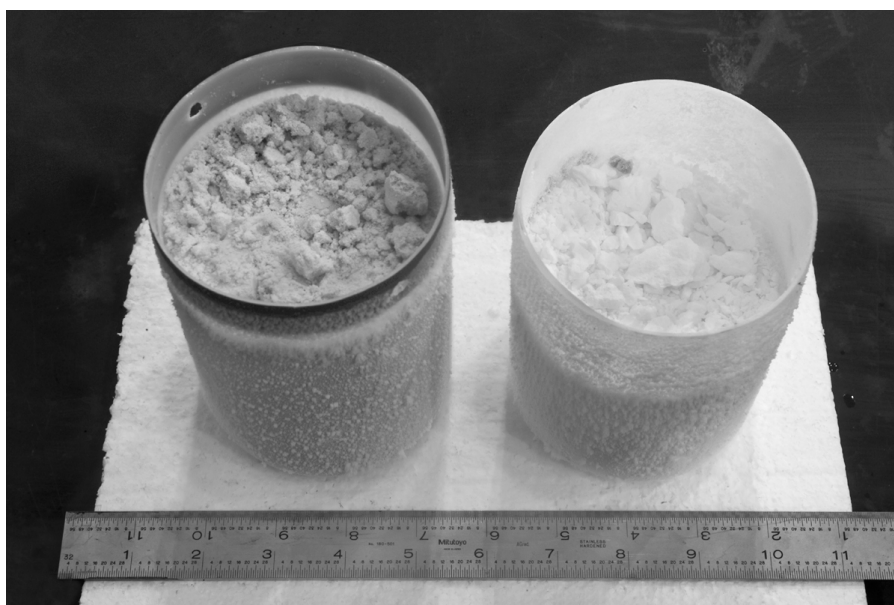


Figure 1. Methane hydrate made in partially saturated sand (l) and pure methane hydrate (r). Scale is in inches.

Our goals include making measurements suitable for validation of numerical codes, and developing techniques that will be useful for measurements on natural samples. Measurements required under steady and phase change conditions include thermal conductivity, permeability, relative permeability, and the kinetics of hydrate formation and dissociation. To date, we have performed several tests to evaluate the repeatability of hydrate formation in partially saturated sand, followed by thermal or pressure-induced dissociation. An example of one step of a multiple step thermal dissociation of a hydrate/sand sample is presented in Figure 2. Thermocouples were located at the midplane of the cylindrical sample at the sample edge (inner edge of the pressure vessel), at the half radius, and at the center (Figure 3). The temperature was changed by increasing the temperature of the bath in which the pressure vessel was submerged. In Figure 2, 0.16 moles of methane were released (of the approximately 1.9 moles of methane contained in hydrate initially) as a response to this 0.5 °C temperature increase causing a roughly 0.5 MPa pressure increase in the vessel.

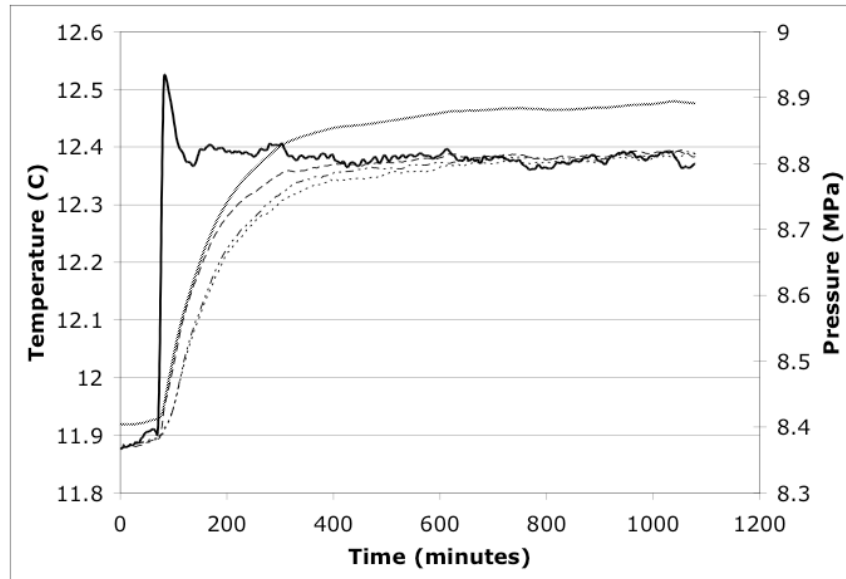


Figure 2. Thermally induced dissociation step. Temperature in the bath (solid black), at the vessel/sample interface (large dash), half radius (mixed long and short dashes), center (small dash), and pressure (gray) recorded in thermal dissociation of 10 cm diameter, 11 cm long sand/hydrate sample.

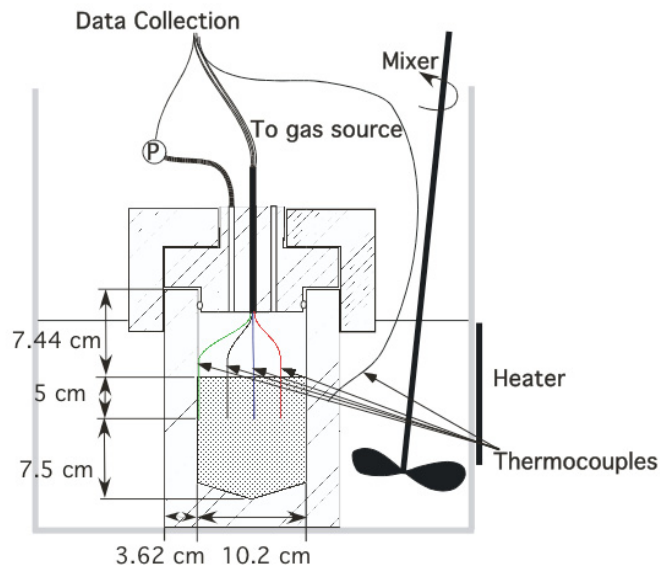


Figure 3. Pressure vessel, bath, and thermocouple configuration. The bath is housed in a freezer.

Dissociation events induced by reducing pressure were accompanied by strong cooling due to the endothermic nature of dissociation, and the release of gas (Joule-Thompson effect) (Figure 4).

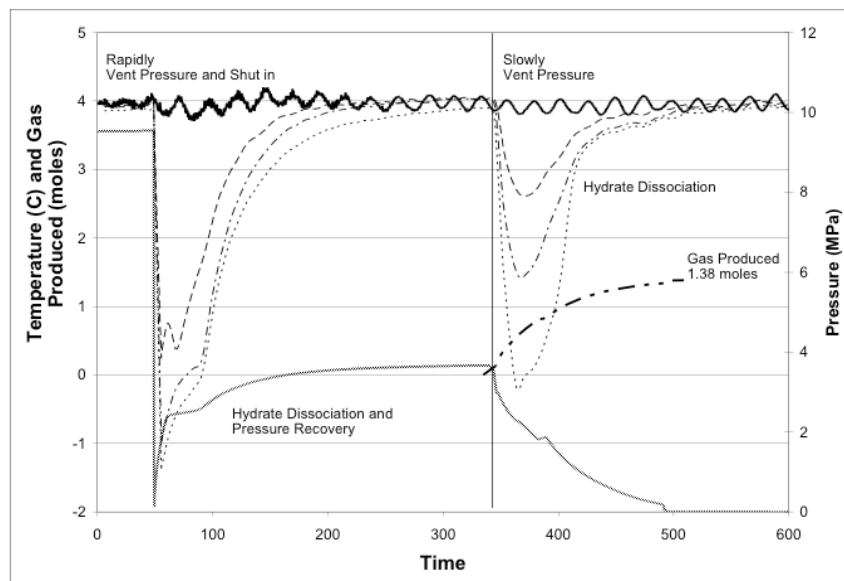


Figure 4. Pressure induced methane hydrate dissociation. Temperature in the bath (solid black), at vessel/sample interface (large dash), half radius (mixed long and short dashes), center (small dash), and pressure (gray) recorded in pressure-induced dissociation of 10 cm diameter, 11 cm long sand/hydrate sample. The gas produced is shown in the thick mixed dash line on the right half of the figure (read on left axis).

More measurements of laboratory-made hydrate samples in various configurations are needed to better constrain numerical models of natural gas production from hydrate-bearing reservoirs. We have begun making samples of sufficient size and perform tests useful for model validation. Robust techniques needed to examine and make measurements on painstakingly collected and preserved natural hydrate-bearing samples must be developed through careful experimentation using laboratory samples.

- Sloan, E.D., Jr., 1998. Clathrate hydrates of natural gases, second edition, revised and expanded. Marcel Dekker, NY, 754 pp.
- Stern, L.A., Kirby, S.H. and Durham, W.B., 1998. Polycrystalline methane hydrate: Synthesis from superheated ice, and low-temperature mechanical properties. *Energy & Fuels*, 12(2): 201-211.